International Journal of Solids and Structures 46 (2009) 271–286

Contents lists available at ScienceDirect

International Journal of Solids and Structures

journal homepage: www.elsevier.com/locate/ijsolstr

Heuristic search for a predictive strain-energy function in nonlinear elasticity

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ARTICLE INFO

Article history:
Received 13 March 2008
Received in revised form 27 June 2008
Available online 10 September 2008

Keywords:
Deformation
Constitutive behaviour
Polymeric material
Polymer network
Finite strain

ABSTRACT

In this work, a new, quasi-structural model – bootstrapped eight-chain model – is proposed as a modification to the strain energy of eight-chain model [Arruda, E.M., Boyce, M.C., 1993. A three-dimensional constitutive model for the large stretch behaviour of rubber elastic materials. J. Mech. Phys. Solids 41, 389—412] that invokes the Langevin chain statistics. This development has been led to by our heuristic search into how the strain energy of eight-chain model may be adapted in order to account better for the mechanical behaviour of elastomeric materials in both linear and nonlinear elastic regimes [Treloar, L.R.G., 1944. Stress–strain data for vulcanised rubber under various types of deformation. Trans. Faraday Soc. 40, 59–70]. The eight-chain model appears to produce very similar results in predicting biaxial stress to those of a first stretch-invariant model that gives a good fit in uniaxial extension and, thus, it is shown that the former can not be significantly enhanced within the limitation of the latter. Evaluation of predictive capability for an additive invariant-separated form of strain energy shows that an explicit inclusion of a second stretch-invariant function would not work and that any thus added term ought to be dependent on both the first and second stretch-invariants of deformation tensor, and hints that an improvement is possibly needed at low strain. The composite and filament models [Miroshnychenko, D., Green, W.A., Turner, D.M., 2005. Composite and filament models for the mechanical behaviour of elastomeric materials. J. Mech. Phys. Solids 53 (4), 748–770] have their strain-energy functions in that suggested form and cope very well with predicting the experimental data of Treloar (1944). We use the form of strain energy for the filament model, that proved to be successful, to bootstrap the strain energy of eight-chain model in order to improve the performance of the latter at low strain. Thus, we derive a new model – bootstrapped eight-chain model – that requires only two material parameters – a rubber modulus and a limiting chain extensibility. The proposed model is quasi-structural due to bootstrapping and it retains the best traits and corrects the faults of the eight-chain model, conforming more closely to the classical experimental data of Treloar (1944).

1. Introduction

In nonlinear elasticity, the experimental data due to Treloar (1944) is widely regarded as a benchmark for the mechanical behaviour of elastomeric materials. This set of experimental data provides the results of measurements on 8% sulphur rubber for engineering stresses in pure shear, equibiaxial extension, and uniaxial elongation (Fig. 1). A particular advantage of this set is that the range of deformation achieved in the experiments is large not only in uniaxial extension (up to stretches of

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0020-7683/$ - see front matter
doi:10.1016/j.ijsolstr.2008.08.037

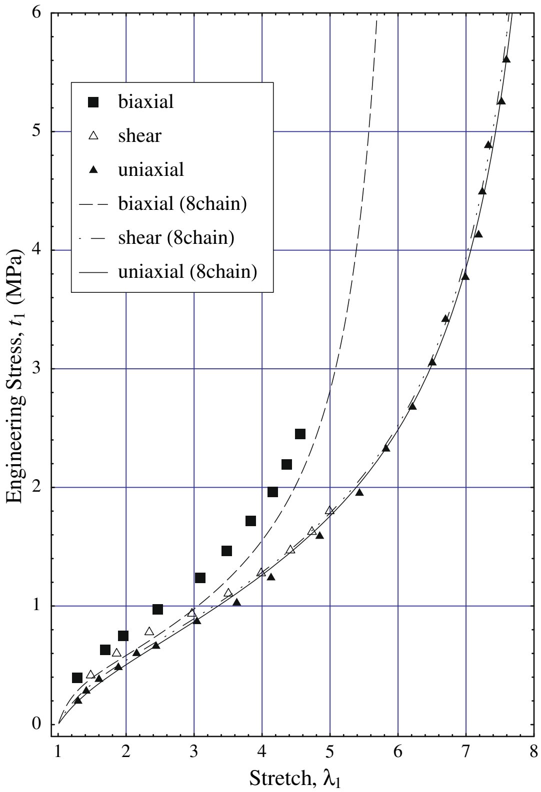

Fig. 1. The prediction of the engineering stress by the eight-chain model (Arruda and Boyce, 1993) in three basic deformation states vs. the experimental data of Treloar (1944).

about $\lambda_1 = 7.6$) but also in equibiaxial one ($\lambda_1 = 4.6$). With a relative shortage of experimental evidence in the literature on rubberlike materials in different deformation states at very large stretches, authors traditionally use the data of Treloar (1944) for testing their models and also for comparison with other models. These experimental results are also representative of those for many other rubberlike materials and, thus, are considered by many to be exceptionally valuable.

Some successful models do exist that can reproduce the stress–stretch curve in one (say, uniaxial) type of tension very well but would struggle subsequently to predict accurately enough the stress in other (biaxial, in particular) types of deformation. Therefore, significant improvement is critically needed in order to better cope with characterisation and prediction of data such as (Treloar's, 1944), especially in equibiaxial extension. A better model capable of predicting performance of polymer materials in deformation more reliably may facilitate the enhancement of existing and development of future production processes in industry and can improve our theoretical understanding of nonlinear elasticity.

We discern between the phenomenological and structural modelling. Both lead to constitutive equations for isotropic, incompressible and nonlinear elastic materials derived usually through identifying a strain-energy function. Phenomenological models are based on empirical evidence and mathematical developments that give the strain energy as a function either of invariants of the deformation tensor or as a function of principal stretches. Structural models are derived from physical considerations that relate the macroscopic behaviour of rubberlike materials to deformations in their polymer networks. Such a derivation also leads to a strain-energy function and relies on choosing a certain kind of chain statistics (Treloar, 1975). Structural models are, thus, based directly on the underlying physical mechanisms of material deformation and as such may be regarded to be predictive with a higher degree of confidence than phenomenological models. The former can also be viewed as more reliable in general or in some situations even preferred to the latter.

A review of phenomenological and structural models can be found in Boyce and Arruda (2000), Marckmann et al. (2002), Ogden et al. (2006) or Miroshnychenko et al. (2005). In the latter, we indicate that the other authors consider the most effective, successful and simple ones among those to date to be the eight-chain model (Arruda and Boyce, 1993) and the Ogden (1972) model. These models have certain advantages as well as some shortcomings that we also mentioned there.

The most effective phenomenological model that is due to Ogden (1972) may basically fit any set of experimental data. However, it may require a large number of parameters to capture the material behaviour. In the case of the Treloar (1944) data, it involved a three-term energy function (Ogden, 1972) that required six material constants and the fit was based on the all three sets of data. Moreover, it can be noted that to perform better it may need an additional, fourth term for the strain-energy function (Ogden, 2007).

In contrast, the most successful structural model – the eight-chain model – uses only two physical constants to characterise a polymer material. The eight-chain model (Arruda and Boyce, 1993) can capture the highly nonlinear elastic behaviour of rubberlike materials (Treloar, 1944) rather well in uniaxial extension but will allow for large deviations in subsequent prediction of engineering stress in equibiaxial extension. That may be due to a difficulty (Boyce and Arruda, 2000) of the eight-chain model in describing the mechanical behaviour of polymers at low strain.

A few modifications to the strain energy of eight-chain model were proposed (Wu and van der Giessen, 1993; Boyce and Arruda, 2000; Meissner and Matejka, 2003). However, those either have several more material parameters, or show large deviations at low strain, or are outperformed by the eight-chain model itself. Furthermore, those modifications were not suggested on the basis of an heuristic evaluation of the predictive capability of the eight-chain model that we offer here.

In this paper, we report our heuristic findings (Miroshnychenko, 2002) suggesting as well that the relevant modification might indeed be needed for the area of small stretches. First, we compare the predictive ability of the eight-chain model (Arruda and Boyce, 1993) with that of a first stretch-invariant model. A more general approach would be to assume that the strain energy depends on both the first and second invariants of deformation tensor and it is necessary to adopt this general form of dependence in the light of the experimental results. Thus, secondly, we consider an additive form of the stain energy that involves two functions – one dependent on the first invariant and the other on the second invariant of deformation tensor. We evaluate a possibility to adapt the strain energy function of the eight-chain model into this additive invariant-separated form by assuming a linear relation between the former and the first stretch-invariant function of the latter. All model evaluations are based on the experimental data due to Treloar (1944).

The semi-phenomenological and semi-structural composite model that was proposed (Miroshnychenko et al., 2005) can overcome that difficulty that the eight-chain model has at low strain. The composite model generates its constitutive equations by combining the approach of Poisson's function with the filament theory and the model requires only three material parameters. We also identified the strain energy function. Furthermore, simple asymptotic consideration allowed us to reduce the number of material constants to just two, thus, forming a new model – filament model. This filament model reflects a common macromolecular origin (nature) that linear elastic deformation has with the orientational effects on polymer chains in nonlinear regime.

The composite model was the main development there (Miroshnychenko et al., 2005), whereas the filament model was proposed to test indirectly a possibility of deriving a structural model with only two material constants that would perform adequately. A close agreement between the filament model and the experiments suggests strongly that it is feasible and that such a structural model will possibly be a modification to the eight-chain model. In this paper, therefore, we propose a predictive strain energy function that such a model may have and be successful. This strain energy will be identified through bootstrapping the strain energy function of the eight-chain model. Thus, the newly found bootstrapped eight-chain model may be regarded as quasi-structural.

2. Eight-chain model and its evaluation

Constitutive equations can be expressed through the work of deformation or the strain energy (Ogden, 1997). This determines the stress–stretch relations for isotropic, incompressible and nonlinear elastic materials to within an arbitrary hydrostatic pressure p in the form

$$\boldsymbol{\sigma} = -p\mathbf{I} + 2\mathbf{B}\frac{\partial W}{\partial \mathbf{B}}, \tag{1}$$

where $\boldsymbol{\sigma}$ is the stress tensor, $\mathbf{I}$ is the identity tensor, and $\mathbf{B}$ stands for the left Cauchy–Green deformation tensor. The stress–strain relation is automatically determined once a function W for the strain energy is identified. The choice is generally unrestricted but not completely.

The interrelationship of different types of strain for isotropic and incompressible materials can be conveyed through a general form of the strain energy

$$W = W(I_1, I_2), \tag{2}$$

in terms of the first two stretch-invariants of deformation tensor $\mathbf{B}$:

$$\begin{aligned} I_1 &= \lambda_1^2 + \lambda_2^2 + \lambda_3^2, \\ I_2 &= \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2, \\ I_3 &= \lambda_1^2\lambda_2^2\lambda_3^2, \end{aligned}$$

where $\lambda_1, \lambda_2, \lambda_3$ are the three principal stretches. The third stretch-invariant $I_3 = 1$ in view of the assumed condition of material incompressibility

$$\lambda_1\lambda_2\lambda_3 = 1.$$

The form (2) gives still a very wide scope for the theory to cover, though we need it be sufficiently specific to be of real value. This is where the modelling comes in.

The model in focus is that due to Arruda and Boyce (1993) who proposed the three-dimensional constitutive equations that model well the mechanical response of rubberlike materials to large elastic deformation. The underlying macromolecular network structure in such materials can be characterised by the non-Gaussian behaviour of its individual chains. Their model is based on an eight-chain representation of the full network. It is believed that this representation captures quite accurately the cooperative nature of polymer chain network in deformation. The strain-energy function of the eight-chain model is dependent on the first invariant of Cauchy–Green deformation tensor only, and it requires only two material parameters – a rubber modulus and a limiting chain extensibility.

All chain vectors in the given configuration (Arruda and Boyce, 1993) have the same lengths regardless of a deformation state. Each chain in the system undergoes a stretch

$$\lambda_{\text{chain}} = \sqrt{\frac{\lambda_1^2+\lambda_2^2+\lambda_3^2}{3}} = \sqrt{\frac{I_1}{3}}, \tag{3}$$

equivalent to that in every other chain of the network, and therefore the model is likened to averaging the contributions of a single chain over the eight spatial orientations.

The eight-chain model exploits the Langevin chain statistics for describing the reduction in entropy on stretching a single chain from the unstretched state that is representative for any of the eight chains in the model network. The work of deformation $W_{8\text{ch}}$ is, thus, written in terms of the chain stretch λ_{chain} in the form:

$$W = W_{8\text{ch}}\left(\frac{\lambda_{\text{chain}}}{\sqrt{N}}\right) = nk_{\text{B}}TN\left(\frac{\lambda_{\text{chain}}}{\sqrt{N}}\beta + \ln\frac{\beta}{\sinh\beta}\right) - Tc', \tag{4}$$

where n is the chain density, k_{B} is Boltzmann's constant, T is the temperature, N is the number of statistical links in a chain, and c' is a constant. Here, β is the inverse Langevin function given as

$$\beta = \mathscr{L}^{-1}\left(\frac{\lambda_{\text{chain}}}{\sqrt{N}}\right), \quad \mathscr{L}(\beta) = \coth\beta - \frac{1}{\beta}.$$

The use of Langevin (non-Gaussian) statistics properly accounts for the limiting chain extensibility, $\lambda_{\text{L}} = \sqrt{N}$ also known as a locking stretch. The rubber modulus is known as $C_{\text{R}} = nk_{\text{B}}T$.

The strain energy (4) yields, upon its substitution into (1), the constitutive equations for the eight-chain model and these can be written in terms of the difference of two principal stresses as

$$\begin{aligned}
\sigma_1 - \sigma_3 &= \lambda_1\frac{\partial W}{\partial\lambda_1} - \lambda_3\frac{\partial W}{\partial\lambda_3} = \frac{nk_{\text{B}}T}{3}\sqrt{N}\mathscr{L}^{-1}\left[\frac{\lambda_{\text{chain}}}{\sqrt{N}}\right]\frac{\lambda_1^2-\lambda_3^2}{\lambda_{\text{chain}}},\\
\sigma_2 - \sigma_3 &= \lambda_2\frac{\partial W}{\partial\lambda_2} - \lambda_3\frac{\partial W}{\partial\lambda_3} = \frac{nk_{\text{B}}T}{3}\sqrt{N}\mathscr{L}^{-1}\left[\frac{\lambda_{\text{chain}}}{\sqrt{N}}\right]\frac{\lambda_2^2-\lambda_3^2}{\lambda_{\text{chain}}}.
\end{aligned} \tag{5}$$

These relations (5) exhibit the characteristic stress–stretch dependence in nonlinear regime.

Arruda and Boyce (1993) compared the predictive capability of their eight-chain model (5) with that of several other prominent models and claimed the simplicity and effectiveness of their model over the earlier ones. Only the Ogden (1972) model was cited capable to better predict the mechanical response of rubber materials (Treloar, 1944). However, in order to capture this nonlinear behaviour, the Ogden model requires six material parameters in juxtaposition with only two of the eight-chain model.

The eight-chain model (5) is found to predict the response of rubberlike materials (Treloar, 1944) quite accurately in uniaxial extension and pure shear, and better than other models in equibiaxial extension (Fig. 1). However, there is still a considerable discrepancy between the prediction and experiment in equibiaxial deformation. The relative standard deviation (Table 3) in equibiaxial extension amounts to 20.13%, which is still substantially excessive.

We single out the eight-chain model (5) for our study in this paper and the section, and we use its form of strain energy as the backbone in our search for a predictive strain-energy function. The chain stretch (3) in this network model is a root-mean-square of the applied stretches so that the strain energy (5) of the eight-chain model appears as a function of the first stretch-invariant I_1 only. In our heuristic search, let us now evaluate the possibility if some strain-energy function, dependent on the first invariant of Cauchy–Green deformation tensor only, could facilitate a better fit with the Treloar (1944) experimental data.

2.1. First stretch-invariant model

Herein, we juxtapose the strain-energy function of eight-chain model (Arruda and Boyce, 1993) with that of an arbitrary first stretch-invariant model:

$$W = W(I_1). \tag{6}$$

In general, we would like to evaluate the possibility that some form of strain energy (6) might produce better prediction of the Treloar (1944) experimental data in equibiaxial extension. In particular, we exploit the experimental data due to Treloar

(1944) for uniaxial extension to predict the engineering stress in equibiaxial extension on the basis of (6). Then, we compare the predicted values of stress with the results of the eight-chain model and of the experiments on equibiaxial extension.

The rationale of this method (Miroshnychenko, 2002) is based on the fact that the the eight-chain model gives quite accurate agreement (Fig. 1, Table 3) with the Treloar (1944) experimental data in uniaxial extension. Thus, it is reasonable to expect that a possible better first stretch-invariant model (6) may also perform well predicting engineering stresses in this deformation state. Hence, the engineering stress can be predicted theoretically for biaxial extension on the basis of (6) and available experimental data on uniaxial tests.

We can rewrite the stress–strain relation (1) in terms of the derivative of strain energy with respect to the first stretch-invariant as

$$\sigma_j = -p + 2\lambda_j^2 W'_{\mathrm{exp}}(I_1) \quad (j = 1,2,3).$$

Here, the index in W'_{exp} refers to experiment based values found further.

In uniaxial extension

$$\lambda_1 = \lambda_{\mathrm{U}} > 1, \quad \lambda_2 = \lambda_3 = 1/\sqrt{\lambda_{\mathrm{U}}},$$

the principal stresses are given by

$$\sigma_1 = 2(\lambda_{\mathrm{U}}^2 - 1/\lambda_{\mathrm{U}}) W'_{\mathrm{exp}}(I_1^{\mathrm{U}}), \quad \sigma_2 = \sigma_3 = 0, \tag{7}$$

and the first stretch-invariant has the form

$$I_1^{\mathrm{U}} = \lambda_{\mathrm{U}}^2 + 2/\lambda_{\mathrm{U}}. \tag{8}$$

Here, a text index indicates a type of tension: U for uniaxial, B for biaxial. The engineering stress $t(\lambda_{\mathrm{U}}) = t_{\mathrm{U}}$ corresponds to $\sigma_1/\lambda_{\mathrm{U}}$, and the Eq. (7) gives

$$W'_{\mathrm{exp}}(I_1^{\mathrm{U}}) = \frac{t_{\mathrm{U}}}{2(\lambda_{\mathrm{U}} - 1/\lambda_{\mathrm{U}}^2)}. \tag{9}$$

This expression (9) provides us with the values of strain-energy derivative at certain points $I_1 = I_1^{\mathrm{U}}$. We can find a principal stretch in equibiaxial extension

$$\lambda_1 = \lambda_2 = \lambda_{\mathrm{B}} > 1, \quad \lambda_3 = 1/\lambda_{\mathrm{B}}^2$$

such that it gives the same value for the first stretch-invariant

$$I_1^{\mathrm{B}} = 2\lambda_{\mathrm{B}}^2 + 1/\lambda_{\mathrm{B}}^4 \tag{10}$$

as the one (8) in uniaxial extension. This will allow us to calculate the principal stresses in equibiaxial deformation at certain points.

Hence, equating (8) and (10)

$$2\lambda_{\mathrm{B}}^2 + 1/\lambda_{\mathrm{B}}^4 = I_1^{\mathrm{B}} = I_1^{\mathrm{U}} = \lambda_{\mathrm{U}}^2 + 2/\lambda_{\mathrm{U}},$$

we find the corresponding stretch in equibiaxial extension to be

$$\lambda_{\mathrm{B}} = \frac{\lambda_{\mathrm{U}}}{2}\sqrt{1 + \sqrt{1 + \frac{8}{\lambda_{\mathrm{U}}^3}}} > 1, \tag{11}$$

while the other roots are not relevant being either negative or complex, or of no interest here corresponding to biaxial compression ($\lambda_{\mathrm{B}} = 1/\sqrt{\lambda_{\mathrm{U}}} < 1$).

Thus, using the value of strain-energy derivative (9) found for uniaxial extension, we have the formulae for the stress in equibiaxial extension (11) as

$$\sigma_1 = \sigma_2 = 2(\lambda_{\mathrm{B}}^2 - 1/\lambda_{\mathrm{B}}^4) W'_{\mathrm{exp}}(I_1^{\mathrm{U}}), \quad \sigma_3 = 0.$$

The corresponding engineering stress $t(\lambda_{\mathrm{B}}) = t_{\mathrm{B}}$ can, hence, be expressed as

$$t_{\mathrm{B}} = \sigma_1/\lambda_{\mathrm{B}} = 2(\lambda_{\mathrm{B}} - 1/\lambda_{\mathrm{B}}^5) W'_{\mathrm{exp}}(I_1^{\mathrm{U}}). \tag{12}$$

In Table 1, we present the experimental data λ_{U} and t_{U} on uniaxial tests taken from Treloar (1944), the values for the first stretch-invariant I_1^{U} and the strain-energy derivative $W'_{\mathrm{exp}}(I_1^{\mathrm{U}})$ given by (8) and (9) respectively, and the corresponding equibiaxial stretch λ_{B} and engineering stress t_{B} given by (11) and (12).

In Fig. 2, we present experimental values of engineering stress in equibiaxial extension from Treloar (1944), their prediction (Table 1) on the basis of (6) and the experimental data on uniaxial tests (Treloar, 1944), and the corresponding predictions by the eight-chain model (4).

Table 1
The equibiaxial stretch λ_B and engineering stress t_B calculated from (11) and (12) using the experimental data λ_U and t_U on uniaxial tests from Treloar (1944)

Uniaxial extension		Strain energy		Biaxial extension	
λ_U	t_U (MPa)	I_1^U	$W'_{exp}(I_1^U)$	λ_B	t_B (MPa)
1.293	0.198	3.219	0.142	1.151	0.187
1.414	0.283	3.414	0.155	1.216	0.260
1.601	0.382	3.812	0.158	1.320	0.337
1.886	0.482	4.617	0.150	1.485	0.405
2.155	0.600	5.572	0.155	1.649	0.487
2.440	0.661	6.773	0.145	1.828	0.518
3.042	0.869	9.911	0.148	2.222	0.653
3.628	1.026	13.714	0.144	2.617	0.753
4.132	1.238	17.558	0.152	2.962	0.899
4.848	1.588	23.916	0.165	3.458	1.142
5.433	1.951	29.886	0.181	3.865	1.396
5.823	2.324	34.251	0.201	4.138	1.660
6.213	2.677	38.923	0.216	4.411	1.908
6.505	3.050	42.623	0.235	4.616	2.172
6.699	3.417	45.172	0.256	4.753	2.432
6.991	3.771	49.160	0.270	4.958	2.682
7.185	4.129	51.903	0.288	5.094	2.935
7.240	4.492	52.694	0.311	5.133	3.193
7.328	4.883	53.973	0.334	5.195	3.470
7.522	5.251	56.846	0.350	5.331	3.730
7.594	5.604	57.932	0.370	5.382	3.981

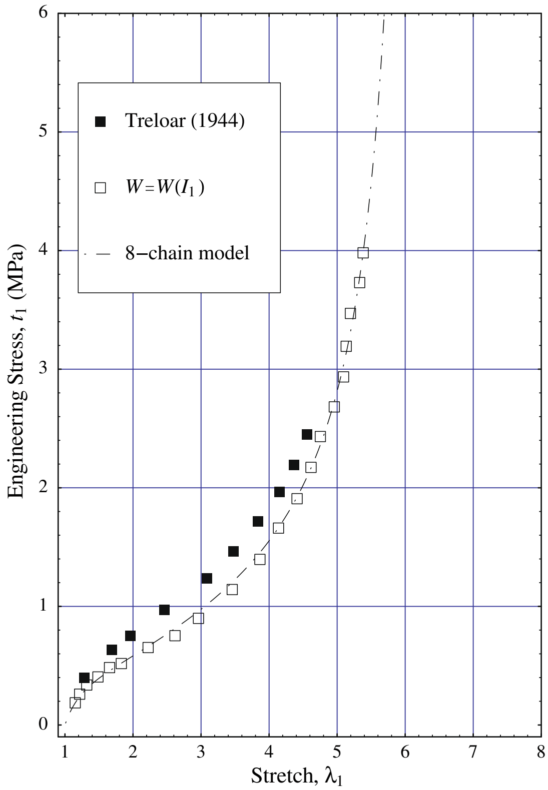

Fig. 2. Comparison of the results of eight-chain model (4) and of a first stretch-invariant model (6) in predicting the engineering stress in equibiaxial extension from Treloar (1944).

From Fig. 2, one can see that the predictions by the eight-chain model (Arruda and Boyce, 1993) are very close to those of a first stretch-invariant model (6). In fact, the relative standard deviation between these predictions is only within the range of 6.84–7.89% that is to be contrasted with the discrepancy of 20.13% for the eight-chain model in predicting the experimental data in equibiaxial extension from Treloar (1944).

These results mean, on the one hand, that the strain-energy function (4) due to the eight-chain model offers almost the utmost in predictive capability amongst all possible models, whose strain energy belongs to the class of functions (6). On the other hand, these results indicate only a possibility of a slight improvement on the performance of the eight-chain model within that functional class (6).

This comparison reveals that, in order to capture more accurately the mechanical behaviour of rubberlike materials, it is necessary to consider a more general class of strain-energy functions (2) than that limited by (6). This is also further supported by the considerations in Hart-Smith (1966) and in Wineman (2005). In our heuristic search, let us now evaluate the possibility if a simpler form of strain-energy function – an additive form that separates the dependence on the two invariants of deformation tensor – could lead to a better agreement with the experimental data of Treloar (1944).

2.2. Additive invariant-separated form

On the one hand, additive separable strain-energy forms (e.g. Mooney, 1940; Valanis and Landel, 1967) proved to be quite popular because of their mathematical simplicity. On the other hand, physical considerations involving calculation of entropy may also lead to an additive separable form for the strain energy, e.g. James and Guth (1943), Wang and Guth (1952). Therefore, we propose to consider a simplification of (2) such that the dependence on the stretch-invariants may be separated into the additive form:

$$W = W_1(I_1) + W_2(I_2), \tag{13}$$

which is both simple mathematically and plausible from the physical point of view.

We have established that the strain energy (4) due to the eight-chain model performs exceptionally well within the limits of functional class (6). In our heuristic search for a predictive strain-energy function, we try and adhere as close as possible to structural modelling. This together with the fact above suggests that we may assume a relation between the first function on the right-hand side of (13) and the strain energy (4). Further, herein we adopt the following linear formula:

$$W_1(I_1) = \alpha W_{8\mathrm{ch}^*}(I_1), \tag{14}$$

where the parameter α is to be determined, and, for convenience, the notation has been changed meaning $W_{8\mathrm{ch}^*}(I_1) = W_{8\mathrm{ch}}\left(\lambda_{\mathrm{chain}}/\sqrt{N}\right)$. Note as well that the second function on the right-hand side of (13) represents a phenomenological contribution in general.

We can identify the behaviour of unknown function $W_2(I_2)$ at certain points $I_2 = I_2^{\mathrm{U}}$ in terms of α and values of $W_{8\mathrm{ch}^*}(I_1^{\mathrm{U}})$ taking advantage of the good fit between the predicted stress in uniaxial extension and the experimental data from Treloar (1944). Then, the parameter α can be found fitting the experimental data (Treloar, 1944) in equibiaxial extension.

We can rewrite the stress–strain relation (1) in terms of the derivatives with respect to the first and second stretch-invariants I_1 and I_2 in the form

$$\sigma_j = -p + 2\lambda_j^2 W_1'(I_1) - \frac{2}{\lambda_j^2} W_2'(I_2) \quad (j = 1, 2, 3).$$

In uniaxial extension

$$\lambda_1 = \lambda_{\mathrm{U}} > 1, \lambda_2 = \lambda_3 = 1/\sqrt{\lambda_{\mathrm{U}}},$$

the principal stresses are given by

$$\sigma_1 = 2(\lambda_{\mathrm{U}}^2 - 1/\lambda_{\mathrm{U}})[W_1'(I_1^{\mathrm{U}}) + (1/\lambda_{\mathrm{U}})W_2'(I_2^{\mathrm{U}})], \quad \sigma_2 = \sigma_3 = 0, \tag{15}$$

and the first and second stretch-invariants have the form

$$I_1^{\mathrm{U}} = \lambda_{\mathrm{U}}^2 + 2/\lambda_{\mathrm{U}}, \quad I_2^{\mathrm{U}} = 2\lambda_{\mathrm{U}} + 1/\lambda_{\mathrm{U}}^2.$$

Herein, we use again the fact that the eight-chain model agrees very closely (Fig. 1, Table 3) with the experimental data from Treloar (1944) in uniaxial extension. Thus, it is reasonable to expect that a possible better model (13), (14) may also perform well predicting stress–stretch state in this deformation. Hence, one may assume that the value of the principal stress σ_1 given in (15) corresponds to that of (7) with the substitution of $W'_{\exp}(I_1^{\mathrm{U}}) = W'_{8\mathrm{ch}^*}(I_1^{\mathrm{U}})$.

Equating (15) and (7) as discussed above allows us to characterise the behaviour of the unknown function derivative

$$W_2'(I_2^{\mathrm{U}}) = (1-\alpha)\lambda_{\mathrm{U}} W'_{8\mathrm{ch}^*}(I_1^{\mathrm{U}}) \tag{16}$$

at particular points $I_2 = I_2^{\mathrm{U}}$ in terms of known

$$W'_{8\mathrm{ch}^*}(I_1) = \frac{nk_{\mathrm{B}}T}{3}\sqrt{N}\mathscr{L}^{-1}\left[\frac{\lambda_{\mathrm{chain}}}{\sqrt{N}}\right]\frac{1}{2\lambda_{\mathrm{chain}}}.$$

This provides us with a vehicle to calculate $W_2'(I_2)$ also in equibiaxial extension below exploiting similar idea (Miroshnychenko, 2002) as the one used in the previous subsection.

In equibiaxial extension

$$\lambda_1 = \lambda_2 = \lambda_B > 1, \quad \lambda_3 = 1/\lambda_B^2,$$

the first and second stretch-invariants are

$$I_1^B = 2\lambda_B^2 + 1/\lambda_B^4, \quad I_2^B = \lambda_B^4 + 2/\lambda_B^2,$$

and the principal stresses read

$$\sigma_1 = \sigma_2 = 2(\lambda_B^2 - 1/\lambda_B^4)[W_1'(I_1^B) + \lambda_B^2 W_2'(I_2^B)], \quad \sigma_3 = 0. \tag{17}$$

We can use (16) to compute $W_2'(I_2^B)$ in (17) if we find the principal stretch in uniaxial extension such that

$$\lambda_B^4 + 2/\lambda_B^2 = I_2^B = I_2^U = 2\lambda_U + 1/\lambda_U^2.$$

The corresponding uniaxial stretch has the form

$$\lambda_U = \frac{\lambda_B^4}{4}\left(1 + \sqrt{1 + \frac{8}{\lambda_B^6}}\right) > 1, \tag{18}$$

while the other roots are not relevant being either negative or complex, or of no interest here corresponding to uniaxial compression ($\lambda_U = 1/\lambda_B^2 < 1$).

Consequently, on the basis of (14) and (16), we can rewrite (17) in terms of $W_{8ch^*}'(I_1)$ only as

$$t(\lambda_B, \alpha) = \sigma_1/\lambda_B = 2(\lambda_B - 1/\lambda_B^5)\left[\alpha W_{8ch^*}'(I_1^B) + (1-\alpha)\lambda_B^2\lambda_U W_{8ch^*}'(I_1^U)\right], \tag{19}$$

where λ_U and I_1^U are determined by (18).

We can find the parameter α minimising the square function of standard deviation

$$D(\alpha) = \frac{1}{M}\sum_{\lambda_B}[t_{\exp}(\lambda_B) - t(\lambda_B, \alpha)]^2,$$

where $t_{\exp}(\lambda_B)$ is the Treloar (1944) experimental point for the engineering stress in equibiaxial extension, and $t(\lambda_B, \alpha)$ is given by (19). The least squares best fit $D'(\alpha) = 0$ gives us the value of α dependent on the number of experimental points in equibiaxial extension, M taken into account.

The data in Table 2 clearly shows that the assumption (13) together with (14) can only work up to $\lambda_B = 1.959$. If deformation is taken further, then the limiting material extensibility ($\lambda_U > 7.616$) will be exceeded, and the parameter will tend to

$$\alpha = 1.000. \tag{20}$$

This becomes more evident if, on the basis of (18), we write down the approximate leading order for the expression in square brackets in (19)

$$W_1'(I_1^B) + \lambda_B^2 W_2'(I_2^B) \sim \alpha W_{8ch^*}'(2\lambda_B^2) + (1-\alpha)\frac{\lambda_B^6}{4} W_{8ch^*}'\left(\frac{\lambda_B^8}{16}\right) \quad \text{when } \lambda_B \gg 1.$$

Clearly, the second term above grows much more rapidly compared to the first. That is probably why modifications to the strain energy involving explicitly a function of second stretch-invariant may often not work well (Muhr, 2007). This is also in agreement with the findings by Hart-Smith (1966). However, Table 2 seems also to suggest that improvement for the strain energy of eight-chain model is possible and needed at low strain.

The unit value of parameter (20) means that the invariant-separated functions defined in (14) and (16) become

$$W_1(I_1) = W_{8ch^*}(I_1), \quad W_2(I_2) = 0,$$

Table 2
Approximation of the parameter α by the number of experimental points in equibiaxial extension, M taken into account

Stretch		Function $W_1'(I_1^B)$		Function $W_2'(I_2^B)$				Parameter
M	λ_B	I_1^B	$W_{8ch^*}'(I_1^B)$	$I_2^B = I_2^U$	λ_U	I_1^U	$\lambda_U W_{8ch^*}'(I_1^U)$	α
1	1.284	3.665	0.157	3.931	1.814	4.393	0.260	0.848
2	1.690	5.835	0.153	8.858	4.403	19.841	0.731	0.977
3	1.959	7.743	0.146	15.249	7.616	58.266	2.858	0.995
4	2.463	12.160	0.146	37.131	18.564	344.73	159.72	1.000
5	3.089	19.095	0.155	91.258	45.629	2082.05	69198.7	1.000
6	3.480	24.228	0.166	146.827	73.413	5389.5	$1.9 \cdot 10^6$	1.000
7	3.837	29.450	0.180	216.890	108.445	11760.3	$2.9 \cdot 10^7$	1.000
8	4.154	34.515	0.202	297.880	148.938	22182.5	$2.6 \cdot 10^8$	1.000
9	4.365	38.109	0.213	363.130	181.565	32965.9	$1.1 \cdot 10^9$	1.000
10	4.559	41.571	0.230	432.091	216.045	46675.5	$3.6 \cdot 10^9$	1.000

and this reduces the strain energy (13) to that of the eight-chain model. This result implies that the predictive capability of the eight-chain model cannot be improved within the limitations of (13) and (14). In particular, one has to consider a wider class of functions than that of (13), where

$$W = W_1(I_1) + W_2(I_1, I_2), \tag{21}$$

if a relation of the kind of (14) is to be assumed.

In our heuristic search, we turn to the composite model, whose strain energy is in the class of functions (21), and evaluate if this model could have a high predictive capability fitting the experimental data of Treloar (1944). In the composite model, the second function in (21) comes from a simple linear elastic model, hence, improving the performance at low strain as suggested above, but instead of relation (14) a certain approximation is assumed for the first function in (21).

3. Composite model

The other model in focus is the composite model (Miroshnychenko et al., 2005). This model is capable of describing adequately both linear and nonlinear elastic behaviour of rubberlike materials. The idea of composite model is to combine descriptions for a linear elastic response and for orientational effects on polymer chains in nonlinear regime. Hence, the resulting stress can be given as a composite of linear elastic forces and of nonlinear behaviour and that gave the name to the model. Thus, the overall stress tensor $\boldsymbol{\sigma}$ may be written in an additive form as

$$\boldsymbol{\sigma} = -p\mathbf{I} + \boldsymbol{\sigma}_{\mathrm{p}} + \boldsymbol{\sigma}_{\mathrm{f}},$$

where p denotes a hydrostatic pressure, $\mathbf{I}$ is the identity tensor, $\boldsymbol{\sigma}_{\mathrm{p}}$ stands for the stress due to the approach of Poisson's function and $\boldsymbol{\sigma}_{\mathrm{f}}$ corresponds to the contribution from the filament theory.

The approach of Poisson's function represents a linear element in the model, and it is in essence an extension of Hookean law. The filament theory models the effects of orientation and limiting extensibility of polymer filaments (chains) that is based on a three-dimensional configuration of the eight-chain model. In fact, the filament theory is to some extent an approximation to the behaviour of eight-chain model, and there is a clear analogy between their descriptions that we shall mention later.

The constitutive equations of composite model for rubberlike materials may be given in terms of the difference of two principal stresses as

$$\begin{aligned} \sigma_1 - \sigma_3 &= E\frac{\lambda_1 - \lambda_3}{1+v} + \frac{E_{\mathrm{f}}\lambda_{\mathrm{f}}}{1 - \lambda_{\mathrm{f}}/\lambda_{\max}} \cdot \frac{\lambda_1^2 - \lambda_3^2}{\sqrt{\lambda_1^2 + \lambda_2^2 + \lambda_3^2}}, \\ \sigma_2 - \sigma_3 &= E\frac{\lambda_2 - \lambda_3}{1+v} + \frac{E_{\mathrm{f}}\lambda_{\mathrm{f}}}{1 - \lambda_{\mathrm{f}}/\lambda_{\max}} \cdot \frac{\lambda_2^2 - \lambda_3^2}{\sqrt{\lambda_1^2 + \lambda_2^2 + \lambda_3^2}}. \end{aligned} \tag{22}$$

The quantity v here represents not a material constant (Poisson's ratio) as usual but a variable defined as a symmetrical Poisson's function

$$v = \frac{1}{\lambda_1 + \lambda_2 + \lambda_3 - 1}.$$

Here λ_{f} is a filament stretch given by

$$\lambda_{\mathrm{f}} = \sqrt{\frac{\lambda_1^2 + \lambda_2^2 + \lambda_3^2}{3}}.$$

The composite model (22) operates using three material parameters: Young's modulus E, the filament modulus E_{f}, and the maximum filament stretch $\lambda_{\max}$. The description of composite model indicates that it is semi-phenomenological and semi-structural in its constitution. That combination was a building block for the success of the composite model, which places it near the very top in a model ranking classification (Marckmann and Verron, 2006).

In our previous paper (Miroshnychenko et al., 2005), we presented two formulations of filament stress for the composite model: the e_{f}-formulation based on the filament extension ($e_{\mathrm{f}} = \lambda_{\mathrm{f}} - 1$), proposed by Turner (1997), and the λ_{f}-formulation based on the filament stretch, proposed by us. The two formulations were shown to be quite competitive in predicting different sets of data (Treloar, 1944; Kawabata et al., 1981).

On the one hand, the e_{f}-formulation matched very accurately the experimental data due to Treloar (1944) but, on the other hand, it produced higher errors in comparison with the λ_{f}-formulation while predicting the extensive multiaxial data due to Kawabata et al. (1981). In contrast, our λ_{f}-formulation gave a reasonable fit (Fig. 3, Table 3) to the data of Treloar (1944) and produced a very accurate prediction for the plentiful data of Kawabata et al. (1981). For the filament model discussed here further, the difference in performance of the two formulations was similar in quality. However, even a more striking and successful level of accuracy in predicting the data due to Kawabata et al. (1981) was achieved in the case of the λ_{f}-formulation, and that seals ultimately the 1st rank award to the filament model in the model ranking classification (Marckmann and Verron, 2006).

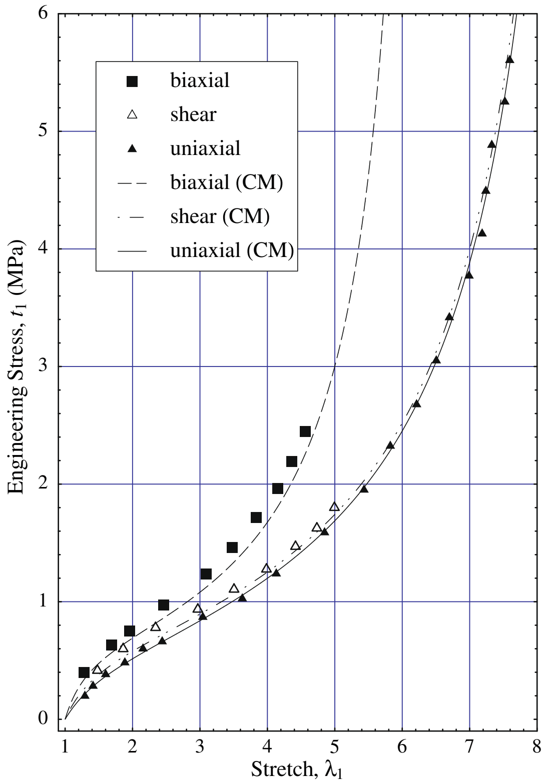

Fig. 3. The prediction of the engineering stress by the composite model (22) in three basic deformation states vs. the experimental data of Treloar (1944).

Table 3
Model parameters fitted to the experimental data due to Treloar (1944) on uniaxial extension and RSD of the models in three basic deformation states

Model	Parameters		RSD (%)		
	C_R (MPa)	N	Uniaxial	Shear	Biaxial
Composite model[a,b]	0.3521	28.270	3.10	7.10	9.99
Filament model[a]	0.2557	24.960	6.30	6.51	9.01
Bootstrapped eight-chain m.	0.2942	27.561	7.23	10.57	9.41
Eight-chain model	0.2774	26.500	4.45	10.39	20.13
Ogden's model			11.18	4.29	4.12

[a] We use the correspondence of parameters here as $C_R = nk_BT = E_f\sqrt{3}$ and $N = \lambda_L^2 = \lambda_{max}^2$.
[b] There is another, third parameter in the composite model: Young's modulus, E. For the Treloar (1944) data, $E = 0.5322$ MPa.

This comparison and the fact that the λ_f-formulation based on the filament stretch comes from an approximation to the inverse Langevin function used in structural models, whereas the e_f-formulation is purely empirical, suggest that the filament stretch formulation will be more reliable in general. Therefore, we restricted our theoretical consideration only to the λ_f-formulation in Miroshnychenko et al. (2005), and that was the leading result there.

The strain energy for the composite model can be expressed as a sum

$$W = W_p + W_f, \tag{23}$$

where W_p represents the contribution from the stress due to the approach of Poisson's function and W_f due to the filament theory. These functions were found to have the forms

$$W_p = E[\lambda_1 + \lambda_2 + \lambda_3 - \ln(\lambda_1 + \lambda_2 + \lambda_3) - 3 + \ln 3], \tag{24}$$

$$W_f = E_f\lambda_{max}^2\sqrt{3}[1 - \lambda_f/\lambda_{max} - \ln(1 - \lambda_f/\lambda_{max}) + c], \tag{25}$$

where c is a constant keeping the strain-energy function zero at $\lambda_f = 1$. Note that Eqs. (23)–(25) belong to the class of functions (21) and that the term W_p is called upon to govern the stress behaviour in the area of small stretches.

Ignoring the constants, the two expressions (24) and (25) represent the same function, $\lambda - \ln\lambda$, but of different variables and with different coefficients. The functional resemblance of (24) and (25) set us thinking about a possibility of elevating the composite model closer to the level of structural models. In our heuristic search, that meant finding a relationship between the material constants and that led to the filament model.

4. Bootstrapped eight-chain model

4.1. Filament model

The filament model (Miroshnychenko et al., 2005) is a bootstrapped filament theory and that fact suggested the name for the model. It is in effect the same composite model only with a reduced number of independent material constants. In the filament model, Young's modulus is related to the other two material parameters through the formula

$$E = E_{\mathrm{f}}\lambda_{\max}. \tag{26}$$

It was derived in an attempt to verify indirectly the possibility that a structural model may be found by a modification to the eight-chain model using additionally the same strain-energy function but of a different variable. And then the filament model may be regarded in some sense as a reflection of that structural model.

The filament model (23)–(26) proved to be very successful (Fig. 4, Table 3). Therefore, we believe that a better structural model than the eight-chain model can be found and that it would also involve additionally the same strain-energy function but of a different variable. For now, it is not yet quite clear how to construct this model using physical considerations that would relate the macroscopic behaviour to material microstructure that is based on the eight-chain configuration. Instead, in our heuristic search, we attempt here to propose a predictive strain-energy function that such a model may have and be successful.

4.2. Bootstrapping

Our task here is to identify that different variable to furnish the following expression for the strain energy

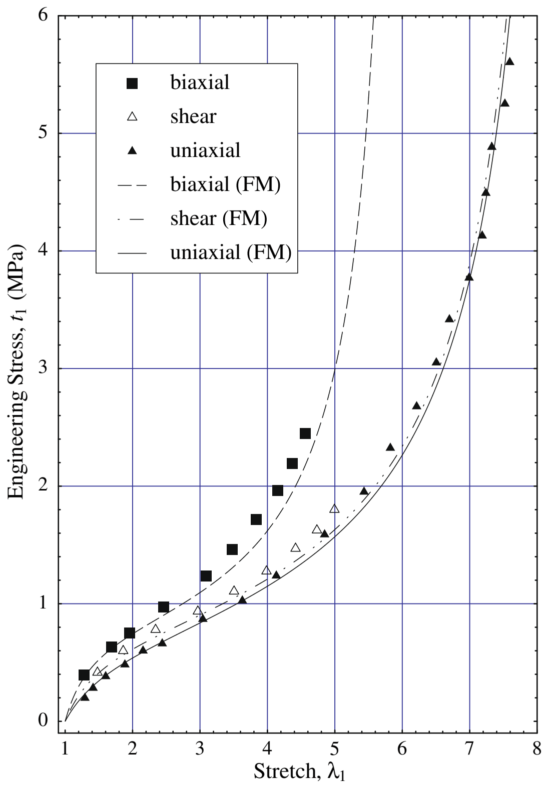

Fig. 4. The prediction of the engineering stress by the filament model (23)–(26) in three basic deformation states vs. the experimental data of Treloar (1944).

$$W = W_{8\mathrm{ch}}(\lambda_{\mathrm{boot}}) + W_{8\mathrm{ch}}\left(\frac{\lambda_{\mathrm{chain}}}{\sqrt{N}}\right), \tag{27}$$

where $W_{8\mathrm{ch}}$ represents the strain-energy function due to the eight-chain model and $W_{8\mathrm{ch}}(\lambda_{\mathrm{boot}})$ is used to indicate the additional term with the unknown different variable denoted by λ_{boot}. The strain energy (27) falls necessarily into the class of functions (21), that is in accord with the conclusions of Section 2. Hence, the sought variable λ_{boot} ought to depend on both the first and second invariants of Cauchy–Green deformation tensor, I_1 and I_2.

On the one hand, it is logical to expect on the basis of (24) that this bootstrapping variable λ_{boot} may involve, in some form, an invariant (Varga, 1966)

$$i_1 = \lambda_1 + \lambda_2 + \lambda_3,$$

which is the first invariant of stretch tensor. Note that it represents a function, though not a simple one, of both the first and second invariants of Cauchy–Green deformation tensor, I_1 and I_2.

However, it is also clear that (27) will not be simply a one-to-one carbon copy of the filament model since the filament theory is only, in some sense, a reflection of the eight-chain model. On the other hand, one may expect the variable λ_{boot} to be comparable in some sense (form or order) to the variable of the other function, $\lambda_{\mathrm{chain}}/\sqrt{N}$. We can identify such a variable by considering the asymptotic behaviour of filament model and mapping it onto the expression (27).

Before that, let us describe the analogy for constants and variables between the filament theory and the eight-chain model (Arruda and Boyce, 1993). The structural model constituents correspond as follows: λ_{f} to λ_{chain}, $\lambda_{\max}$ to $\lambda_{\mathrm{L}} = \sqrt{N}$, and $E_{\mathrm{f}}\sqrt{3}$ to $C_{\mathrm{R}} = nk_{\mathrm{B}}T$.

We apply here a similar reasoning to the one used deriving the filament model (Miroshnychenko et al., 2005). We note the fact that the eight-chain model copes very well with the uniaxial data from Treloar (1944) and, evidently, its strain-energy function does not need any assistance from additional terms in that deformation state at large stretches. In the filament model, that role is played by the logarithmic term in (25).

Hence, we can map the behaviour of the strain-energy function for the eight-chain model (Arruda and Boyce, 1993) to that of the filament theory that describes the exact asymptotic behaviour of the inverse Langevin function at high strain stating that

$$W_{8\mathrm{ch}}\left(\frac{\lambda_{\mathrm{chain}}}{\sqrt{N}}\right) \sim nk_{\mathrm{B}}TN\left[-\ln\left(1-\frac{\lambda_{\mathrm{chain}}}{\sqrt{N}}\right)\right] \mathrm{as}\, \lambda_{\mathrm{chain}} \to \sqrt{N}. \tag{28}$$

Note that the right-hand side in (28) is reminiscent of the strain-energy function in the Gent (1996) model that accounts in a simple way for limiting chain extensibility. This relation (28) is asymptotically exact in the large-stretch limit not only in uniaxial extension but also in any other tensile regime. In fact, the right-hand side in (28) represents a leading approximating term in the filament theory for the strain energy of the eight-chain model at all stretches. We shall use this observation while mapping the behaviour of additional term in (27) onto the rest in (23) with (26).

The rest of the terms in (23) with (26) can give us the expected asymptotic behaviour for the additional term in (27) also at high strain. Thus, we may write that

$$W_{8\mathrm{ch}}(\lambda_{\mathrm{boot}}) \sim nk_{\mathrm{B}}TN\left[\frac{i_1}{\sqrt{3}\sqrt{N}} - \frac{\lambda_{\mathrm{chain}}}{\sqrt{N}}\right] \quad \text{as } \lambda_{\mathrm{chain}} \to \sqrt{N}. \tag{29}$$

The term associated with $-\ln i_1/\sqrt{3N}$ has already been dropped out from the square brackets above because it gives negligible contribution to the stress at high strain. It is also omitted below for consistency reasons as it was neglected while determining the relation (26) that is employed here following the analogy for constants and variables.

The right-hand side of (29) as well as its contribution to the stress would go to zero at high uniaxial strain. This behaviour at high uniaxial strain corresponds to the limiting behaviour of the sought strain-energy function at very small values of variable λ_{boot}

$$W_{8\mathrm{ch}}(\lambda_{\mathrm{boot}}) \sim nk_{\mathrm{B}}TN \cdot \frac{3}{2}\lambda_{\mathrm{boot}}^2 \quad \mathrm{as}\, \lambda_{\mathrm{boot}} \to 0. \tag{30}$$

Of course, the comparison between (29) and (30) may provide us with a certain choice of variable λ_{boot}. However, that choice would conflict with our expectations expressed above that λ_{boot} should be comparable in form or order to the variable $\lambda_{\mathrm{chain}}/\sqrt{N}$ invoked by the second function in (27).

Furthermore, our aim here is to map the behaviour of $W_{8\mathrm{ch}}(\lambda_{\mathrm{boot}})$ onto the relevant terms in the filament model for any tensile regime and not only in the limit of high strain. Therefore, instead, the right-hand side of (29) can serve as an indication for mapping the behaviour at other stretches.

On the one hand, the observation above, that the right-hand side in (28) is a leading approximating term in the filament theory for the strain energy of the eight-chain model at all stretches, and the expected asymptotic behaviour of $W_{8\mathrm{ch}}(\lambda_{\mathrm{boot}})$ at high strain (29) allow us to map asymptotically the behaviour of this additional term in (27) as

$$W_{8\mathrm{ch}}(\lambda_{\mathrm{boot}}) \asymp nk_{\mathrm{B}}TN\left[\frac{i_1}{\sqrt{3}\sqrt{N}} - \frac{\lambda_{\mathrm{chain}}}{\sqrt{N}}\right] \tag{31}$$

for any tensile regime. On the other hand, this behaviour corresponds locally to the limiting behaviour of the sought strain-energy function at small nonzero values of variable λ_{boot}

$$W_{8\text{ch}}(\lambda_{\text{boot}}) \sim nk_{\text{B}}TN\mathscr{L}^{-1}(\lambda)[\lambda_{\text{boot}} - \lambda] \quad \text{as } \lambda_{\text{boot}} \to \lambda \ll 1, \tag{32}$$

where $0 < \lambda \ll 1$ and then $\mathscr{L}^{-1}(\lambda) \sim 3\lambda$.

Hence, the choice becomes rather clear from the comparison of (31) and (32). We suggest that the variable λ_{boot} is simply defined as

$$\lambda_{\text{boot}} = \frac{i_1}{\sqrt{3}\sqrt{N}} - \frac{\lambda_{\text{chain}}}{\sqrt{N}}. \tag{33}$$

The terms in (33) are also comparable, as expected, in form and order to the variable $\lambda_{\text{chain}}/\sqrt{N}$ invoked by the second function in (27).

On the one hand, this choice of variable may give a different asymptotic behaviour (30) at high uniaxial strain to the one expected in (29). However, it will still preserve the vanishing of $W_{8\text{ch}}(\lambda_{\text{boot}})$, as in (29), and of its contribution to the stress at high uniaxial strain. This behaviour will be good enough in that limit. On the other hand, this choice of variable also leads locally to the Hookean behaviour of strain energy at small chain stretches

$$W \sim nk_{\text{B}}TN\mathscr{L}^{-1}(\lambda)\left(\frac{i_1}{\sqrt{3}\sqrt{N}} - 2\lambda\right) \quad \text{as } \frac{\lambda_{\text{chain}}}{\sqrt{N}}, \lambda_{\text{boot}} \to \lambda \ll 1, \tag{34}$$

where $0 < \lambda \ll 1$ and then $\mathscr{L}^{-1}(\lambda) \sim 3\lambda$. This will be an important property of the strain-energy function. Hence, from this point of view, this choice of variable λ_{boot} gives us an ideal mapping to the behaviour of the filament model (23)–(26).

Thus, this choice (33) of variable λ_{boot} defines the strain energy for a new, heuristic model in the form

$$W = W_{8\text{ch}}\left(\frac{i_1}{\sqrt{3}\sqrt{N}} - \frac{\lambda_{\text{chain}}}{\sqrt{N}}\right) + W_{8\text{ch}}\left(\frac{\lambda_{\text{chain}}}{\sqrt{N}}\right). \tag{35}$$

Note that this strain-energy function (35) belongs to the class of functions (21) and that the bootstrapping term supplements the strain-energy in the area of small to moderate stretches.

In some sense, the strain-energy function of the eight-chain model has pulled up itself by its own bootstraps! This gives rise to a new model – bootstrapped eight-chain model. The fact that we have recycled the strain-energy function of the eight-chain model elevates the bootstrapped eight-chain model to the quasi-structural level.

The constitutive equations for the bootstrapped eight-chain model can be written in terms of the difference of two principal stresses as

$$\begin{aligned}
\sigma_1 - \sigma_3 &= nk_{\text{B}}T\sqrt{N}\mathscr{L}^{-1}\left[\frac{i_1}{\sqrt{3}\sqrt{N}} - \frac{\lambda_{\text{chain}}}{\sqrt{N}}\right]\left(\frac{\lambda_1 - \lambda_3}{\sqrt{3}} - \frac{\lambda_1^2 - \lambda_3^2}{3\lambda_{\text{chain}}}\right) + nk_{\text{B}}T\sqrt{N}\mathscr{L}^{-1}\left[\frac{\lambda_{\text{chain}}}{\sqrt{N}}\right]\frac{\lambda_1^2 - \lambda_3^2}{3\lambda_{\text{chain}}}, \\
\sigma_2 - \sigma_3 &= nk_{\text{B}}T\sqrt{N}\mathscr{L}^{-1}\left[\frac{i_1}{\sqrt{3}\sqrt{N}} - \frac{\lambda_{\text{chain}}}{\sqrt{N}}\right]\left(\frac{\lambda_2 - \lambda_3}{\sqrt{3}} - \frac{\lambda_2^2 - \lambda_3^2}{3\lambda_{\text{chain}}}\right) + nk_{\text{B}}T\sqrt{N}\mathscr{L}^{-1}\left[\frac{\lambda_{\text{chain}}}{\sqrt{N}}\right]\frac{\lambda_2^2 - \lambda_3^2}{3\lambda_{\text{chain}}}.
\end{aligned} \tag{36}$$

Note that the model employs only two material parameters – a rubber modulus $C_{\text{R}} = nk_{\text{B}}T$ and a limiting chain extensibility $\lambda_{\text{L}} = \sqrt{N}$.

5. Comparison with other models

Model parameters have been found minimising the relative standard deviation

$$\text{RSD} = \sqrt{\frac{1}{M}\sum_{j=1}^{M}\frac{(\sigma_{\exp j} - \sigma_{\text{th}j})^2}{\sigma_{\exp j}^2}},$$

where M is the number of points in a set of data, $\sigma_{\exp j}$ is an experimental measurement and $\sigma_{\text{th}j}$ its theoretical prediction. We fit the models to the uniaxial data from Treloar (1944) and the determined parameters are listed in Table 3. The parameters used to evaluate relative standard deviations for the eight-chain model and for the Ogden model were taken directly from Arruda and Boyce (1993) and from Ogden (1972) correspondingly.

The predictions of the bootstrapped eight-chain model for the engineering stress from Treloar (1944) are shown in Fig. 5. The agreement with the experimental data in pure shear, uniaxial and equibiaxial extension is very accurate (Table 3).

The bootstrapped eight-chain model performs similarly to the composite and filament models. The filament model produces in some sense the most balanced relative standard deviations in predicting the basic deformation states (Table 3) and gives the least errors in predicting the stress in equibiaxial extension and pure shear. The bootstrapped eight-chain model gives slightly higher errors in the three basic deformations than the composite and filament models except that it does marginally improve on the performance of the composite model in equibiaxial extension. Nonetheless, the errors of the bootstrapped eight-chain model are moderate and the agreement with the experiments is quite satisfactory.

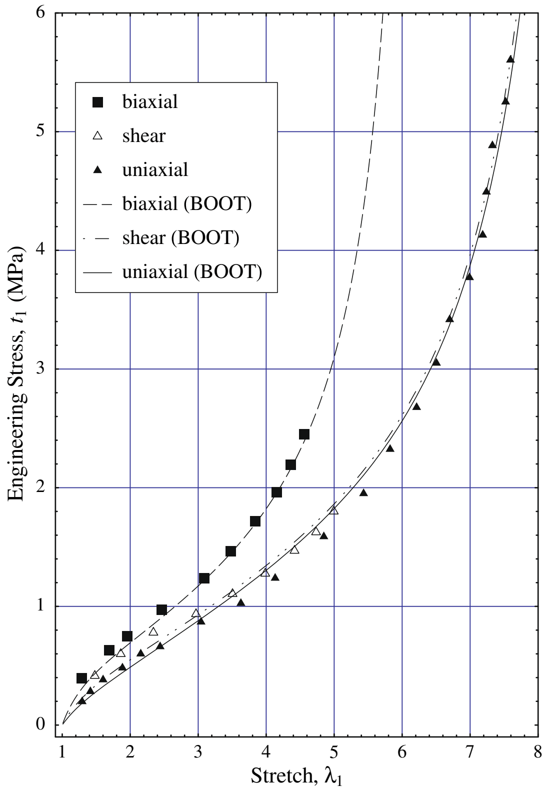

Fig. 5. The prediction of the engineering stress by the bootstrapped 8-chain model (36) in three basic deformation states vs. the experimental data of Treloar (1944).

Furthermore, the bootstrapped eight-chain model re-balances the performance of the eight-chain model (Arruda and Boyce, 1993) in uniaxial and equibiaxial extensions, more than halving the error in the latter deformation state. However, both models seem to suffer similar somewhat higher relative standard deviations in predicting pure shear than the other models considered, although the errors remain within moderate range even in this case. While both models involve non-Gaussian chain statistics describing quite accurately the effects of orientation and limiting extensibility on polymer chains, the bootstrapped eight-chain model is able to overcome the discrepancies that the eight-chain model shows (Boyce and Arruda, 2000; Miroshnychenko, 2002) at small to moderate stretches (i.e., when $\lambda_{chain}/\sqrt{N} \ll 1$). That departure seems to be reasonably well corrected by the bootstrapping term in (35) leading locally to the Hookean behaviour (34) of the total strain energy at small chain stretches. Overall, the bootstrapped eight-chain model conforms more closely to the classical data of Treloar (1944) than the eight-chain model.

The Ogden (1972) model fits the experimental data of Treloar (1944) with relatively moderate errors, but note that model parameters were determined minimising the standard error in all three basic deformations on aggregate. Furthermore, the Ogden model utilises as many as six material constants in this case. However, even with that characterisation, the performance of the Ogden model is comparable to that of the bootstrapped eight-chain model. To perform better, the Ogden model needs to employ a fourth term (Ogden, 2007). Such a term will compensate for the apparent discrepancy (Ogden, 1972) at very high strain in uniaxial tension that is due to the fact that the model does not account for limiting extensibility of polymer chains. The importance of limiting chain extensibility is further stressed in Horgan and Saccomandi (2002), Horgan and Saccomandi (2005).

By and large, the agreement of the bootstrapped eight-chain model with the experimental data of Treloar (1944) is found to be superior than that of the eight-chain model (Arruda and Boyce, 1993) or of the Ogden (1972) model. It is shown that the bootstrapped eight-chain model can perform successfully, employing only two material parameters – a rubber modulus and a limiting chain extensibility. Moreover, this model is quasi-structural and as such it is believed to be very reliable.

6. Conclusions

We have carried out a comprehensive study into how the strain energy of eight-chain model can be adapted to give better agreement in predicting the classical experimental data of Treloar (1944). This our heuristic search has resulted in the new, bootstrapped eight-chain model that is quasi-structural. The constitutive equations of the bootstrapped eight-chain model presented here can be treated easily mathematically and are accessible to an analysis. Moreover, these equations involve only two material parameters, which is minimal, and yet the model appears to outperform the most successful structural (Arruda and Boyce, 1993) or phenomenological (Ogden, 1972) models hitherto in predicting the classical data of Treloar (1944).

In general, we have shown that the bootstrapped eight-chain model is capable to reproduce accurately enough the typical isothermal mechanical response of an isotropic, incompressible rubberlike material (Treloar, 1944) in one state of deformation and then, with that characterisation, to predict successfully other deformation states. In particular, the bootstrapped eight-chain model more than halves the error in predicting the equibiaxial stress–stretch response compared to the eight-chain model, and this constitutes a substantial improvement.

The success of the bootstrapped eight-chain model is due to bootstrapping that allows us to replicate the best traits of the eight-chain model and to correct its faults. The orientational effects and the limiting extensibility of polymer chains (viewed as end-to-end vectors) are represented by the strain-energy function of the eight-chain model. The bootstrapping term is instrumental in accounting more accurately for the stresses at small to moderate stretches, and it also leads locally to the Hookean behaviour of the total strain energy at small chain stretches. Hence, the bootstrapped eight-chain model is free from the shortcomings mentioned above for the Ogden model and for the eight-chain model.

The strain energy ensures the invariance and objectivity of the constitutive equations and is given here explicitly involving the inverse Langevin function that can be calculated without any difficulty these days. This predictive strain-energy function can now be incorporated in programmes employing finite element methods to characterise a polymeric material and to analyse stresses required to bring about further possibly nonuniform deformation.

The development of this quasi-structural, bootstrapped eight-chain model is a very significant and insightful step towards better structural models. It is also quite constructive as it provides a blueprint for deriving a new purely structural model based possibly on the eight-chain configuration. The strain energy of the bootstrapped eight-chain model depends only on the first invariant of Cauchy–Green deformation tensor and on the first stretch-tensor invariant (Varga, 1966). The role of the former variable is known in structural modelling – it determines the description of chain stretch, whereas the role of the bootstrapping variable need yet be identified. It may, however, account for some spatial (three-dimensional) effects as the bootstrapping variable vanishes in a one-dimensional representation that is often used due to viewing a chain as an end-to-end vector while deriving a chain force-stretch relation.

The challenge now is to derive a predictive strain-energy function, using statistical methods, that will describe consistently the structure of a polymer network and its behaviour upon deformation in both linear and nonlinear regimes, and possibly clarify the role of the bootstrapping variable if it appears there. For instance, such a model may be developed allowing, in contrast to the eight-chain model, the position of junction linking the chains together to fluctuate. It is expected that such a model will also involve only a minimal number of material constants and yet give accurate prediction of the experimental data on rubberlike materials, especially in biaxial deformation.

Acknowledgements

The authors thank Wavin Industrial Products Ltd. and Hydro Polymers Ltd. for a partial support of this research in England. The results of this paper were presented at the 6th ICIAM07, Zürich, Switzerland, 15–22 July 2007 and at the 5th ECCMR, Paris, France, 3–8 September 2007, and D.M. would like to thank The Royal Society (UK) and WWTF (Austria) for their financial support at the congress and at the conference respectively.

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